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^{14}C BLANK CORRECTIONS FOR 25–100 μG SAMPLES AT THE NATIONAL OCEAN SCIENCES AMS LABORATORY

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ABSTRACT. Replicate radiocarbon (^{14}C) measurements of organic and inorganic control samples, with known Fraction Modern values in the range Fm = 0–1.5 and mass range 6 μg–2 mg carbon, are used to determine both the mass and radiocarbon content of the blank carbon introduced during sample processing and measurement in our laboratory. These data are used to model, separately for organic and inorganic samples, the blank contribution and subsequently "blank correct" measured unknowns in the mass range 25–100 μg. Data, formulas, and an assessment of the precision and accuracy of the blank correction are presented.

KEYWORDS: AMS, AMS dating, blank corrections.

INTRODUCTION

At the National Ocean Sciences AMS Laboratory (NOSAMS), the ^{14}C concentration of a sample is determined by measuring its carbon isotope abundance ratio with accelerator mass spectrometry (AMS). The Fraction Modern (Fm) of a sample is determined by calculating the deviation of this ratio from that of normalizing standards. In our case, the primary standard is NBS Oxalic Acid I (NIST-SRM-4990) and Modern is defined as 95% of the radiocarbon concentration of NBS Oxalic Acid I normalized to $\delta^{13}C_{VPDB} = -19‰$ (Olsson 1970). Per convention, a correction is made to correct for isotopic fractionation. As such, sample results are corrected to a $\delta^{13}C_{VPDB}$ value of –25‰, assuming a quadratic mass fractionation dependency (Stuiver and Polach, 1977). This correction is made using the AMS measured $^{13}C/^{12}C$ ratio values of the sample and normalizing standards.

At NOSAMS, inorganic samples (e.g., coral, foraminifera, mollusc, sediment [carbonate]) are typically acidified with 100% H_3PO_4, to convert the carbon in the sample to CO_2. Organic samples (e.g., charcoal, plant/wood, sediment [organic]) are typically pretreated and then combusted at high temperature to produce CO_2. Pretreatment of organic samples is usually a series of heated acid-base-acid leaches to remove inorganic carbon and base-soluble organic acids (Gagnon 2000). Regardless of sample type, converted CO_2 is quantified and transferred to a reaction tube for reduction to carbon. Samples having a carbon mass of between 25 and 100 μg are typically reduced on a dedicated "small-sample line" having a reactor volume of 3.92 mL. However, samples as large as 1 mg can be reduced to graphite on this line. CO_2 is reduced using Fe catalyst in the presence of excess hydrogen (Vogel 1987). The majority of our "small samples" are analyzed on the CFAMS system (Roberts 2010) because that system has a higher source-to-detector efficiency than our USAMS system.

Every group of samples analyzed includes concurrently measured secondary standards with consensus Fm values ($Fm_{consensus}$) and appropriate process blanks. Secondary standards include the IAEA C-series reference materials (IAEA 2014) and various materials from the Third, Fourth, and Fifth International Radiocarbon Intercomparison (TIRI, FIRI, and VIRI) exercises (Scott 2003, 2010). Process blank materials include Carrara marble (IAEA C-1) and Icelandic Doublespar (TIRI F) for inorganic carbon samples and acetanilide (CE Elantech, Product # 338.367.00) for organic carbon samples.

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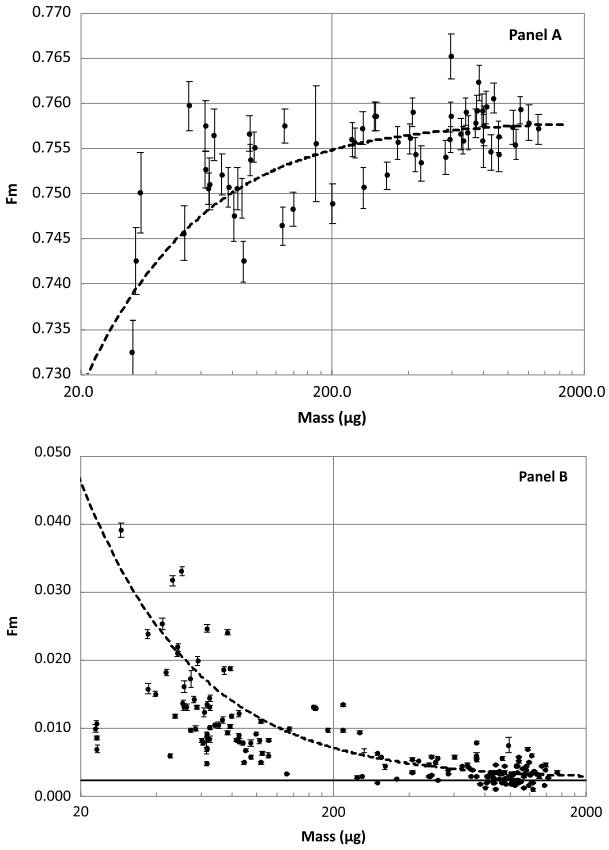

Figure 1 Uncorrected Fm values of FIRI H wood (Panel A, upper plot) and a "radiocarbon-free" acetanilide (Panel B, lower plot) versus manometrically determined sample mass. For the acetanilide, the solid line represents the "large-mass" blank. The dashed lines represent the "mass-balance" blank.

For these secondary standards and blanks, our measured Fm values deviate from expected Fm values as demonstrated in Figure 1. This deviation is most pronounced for small mass samples ($m < 100\,\mu g$) but is present for all sample masses and Fm values. This deviation can be explained by two processes: (1) a "large-mass" blank and (2) a "mass-balance" blank. In the following sections, we present the formulas we use to model these two blank types, details on how we determine the values of the blank contribution (separately for organic and inorganic samples), and subsequently "blank correct" measured unknowns.

BLANK MODEL

The "large-mass" blank manifests itself most clearly for low Fm samples (see Figure 1, Panel B, "radiocarbon-free" sample). The large-mass blank can typically be explained by a combination of one or more of the following: sample pretreatment, carbon contamination in the Fe catalyst used in the reduction step, adsorption of atmospheric CO_2 on to the graphite before it is put under the vacuum of the ion source, ion source memory, or background in the energy spectrum of the AMS ^{14}C detector. The effect of the "large-mass" blank on the Fm of an unknown

sample ($Fm_{unknown}$) can be expressed as:

$$Fm_{measured} = Fm_{unknown} + Fm_{large-blank}\left(1 - \frac{Fm_{unknown}}{Fm_{standard}}\right) \quad (1)$$

where $Fm_{measured}$ is the measured AMS Fm, and $Fm_{large\text{-}blank}$ and $Fm_{standard}$, are the Fm of the "large-mass" blank and primary standard respectively. Equation (1) is effectively the same as Equation (26) in Donahue et al. (Donahue 1990). Conceptually, Equation (1) can be explained as follows: a sample that has the same measured Fm as that of the standard must have an actual Fm equal to that of the standard ($Fm_{measured} = Fm_{standard} \Leftrightarrow Fm_{unknown} = Fm_{standard}$), while a sample that has the same measured Fm as that of the blank must have an actual Fm equal to that of the blank ($Fm_{measured} = Fm_{large\text{-}blank} \Leftrightarrow Fm_{unknown} = 0$).

A "mass-balance" blank reflects the addition of a constant mass contaminant to the sample during sample processing/handling. The modelling of this blank can take the form of a contaminant with a certain mass and Fm (Brown 1997; Hanke 2017) or as a combination of modern and ^{14}C-dead carbon contaminant (Santos 2010; Welte 2018). Both approaches are functionally equivalent. In general, the mass-balance measured Fm ($Fm_{measured}$) of an unknown sample can be expressed as:

$$Fm_{measured} = \frac{Fm_{unknown} \cdot m_{unknown} + Fm_{cont} \cdot m_{cont}}{m_{unknown} + m_{cont}} \quad (2)$$

where $Fm_{unknown}$ and Fm_{cont} are the Fm of the unknown sample and the contaminant, and $m_{unknown}$ and m_{cont} are the mass of the unknown and the contaminant. The form of the "mass balance" blank is represented by dashed lines in Figure 1.

Our procedure to derive a $Fm_{unknown}$ that is corrected for both types of blank is as follows: First, $Fm_{measured}$ values are large-blank corrected by substituting $Fm_{large\text{-}blank\ corrected}$ for $Fm_{unknown}$ into Equation (1):

$$Fm_{large-blank\ corrected} = Fm_{standard}\frac{Fm_{measured} - Fm_{large-blank}}{Fm_{standard} - Fm_{large-blank}} \quad (3)$$

with a corresponding uncertainty of:

$$\delta^2_{Fm_{large-blank\ corrected}} = \left(\frac{Fm_{standard}}{Fm_{standard} - Fm_{large-blank}}\right)^2 \delta^2_{Fm_{measured}} + \left(\frac{Fm_{standard}Fm_{measured} - Fm_{standard}^2}{(Fm_{standard} - Fm_{large-blank})^2}\right)^2 \delta^2_{Fm_{large-blank}} \quad (4)$$

where $\delta_{Fm_{measured}}$, and $\delta_{Fm_{large\text{-}blank}}$ are the uncertainties in the measured and large-blank Fm.

Subsequently, $Fm_{large\text{-}blankcorrected}$ is corrected for mass balance blank by substituting $Fm_{large\text{-}blankcorrected}$ for $Fm_{measured}$ in Equation (2):

$$Fm_{unknown} = \frac{Fm_{large-blank\ corrected}(m_{unknown} + m_{cont}) - Fm_{cont} \cdot m_{cont}}{m_{unknown}} \quad (5)$$

with a corresponding uncertainty of:

$$\delta^2_{Fm_{unknown}} = \left(\frac{m_{unknown} + m_{cont}}{m_{unknown}}\right)^2 \delta^2_{Fm_{large-blank\ corrected}} + \left(\frac{m_{cont}}{m_{unknown}}\right)^2 \delta^2_{Fm_{cont}} + \left(\frac{Fm_{cont}m_{cont} - Fm_{large-blank\ corrected}m_{cont}}{{m_{unknown}}^2}\right)^2 \delta^2_{m_{unknown}} + \left(\frac{Fm_{larg-blank\ corrected} - Fm_{cont}}{m_{unknown}}\right)^2 \delta^2_{m_{cont}} \quad (6)$$

where $\delta_{Fm_{large\text{-}blank\ corrected}}$, $\delta_{Fm_{cont}}$, $\delta_{m_{unknown}}$, and $\delta_{m_{cont}}$ are the uncertainties in the large-blank corrected Fm, contaminant Fm, sample mass, and contaminant mass, respectively.

To determine the values of $Fm_{large\text{-}blank}$, Fm_{cont}, and m_{cont}, we measure and blank correct secondary standards as if they were unknowns. These values are then used to define a total chi-squared statistic:

$$\chi^2 = \frac{1}{N}\sum_{j=1}^{N}\left\{\frac{1}{n}\sum_{i=1}^{n}\frac{(Fm_{unknown_{ji}} - Fm_{consensus_j})^2}{{\sigma_{unknown_{ji}}}^2}\right\} \quad (7)$$

where $Fm_{consensus}$ if the consensus value of the secondary standard, N is the number of unique secondary standards, each having a different consensus value $Fm_{consensus}$, and n is the number of individual measurements of that unique secondary. The χ^2 statistic is initially calculated using starting values of $Fm_{large\text{-}blank}$, Fm_{cont}, and m_{cont}. Then, using the Solver program in Microsoft Excel (2018), we minimize the χ^2 statistic by allowing $Fm_{large\text{–}blank}$, Fm_{cont}, and m_{cont} to vary, subject to certain constraints (e.g., $Fm_{cont} \leq 1$, $m_{cont} > 0$, etc.). In practice, $Fm_{large\text{-}blank}$, Fm_{cont}, and m_{cont} values are different for different samples process types (e.g., organic versus inorganic).

DATA

Figures 2 and 3 show a subset of inorganic and organic secondary standards processed on our small-sample graphitization-line over the past 5 years (2013–2018). Using the measured and consensus Fm values of these secondary standards, we determined $Fm_{large\text{-}blank}$, Fm_{cont}, and m_{cont}, and for inorganic and organic samples by minimizing χ^2 (Equation 7). Resulting $Fm_{large\text{-}blank}$, Fm_{cont}, and m_{cont}, values for inorganic and organic secondary standards are listed in Table 1. No long-term time dependency in the values was observed. The black lines in Figures 2 and 3 show expected $Fm_{measured}$ results using Table 1 blank and mass balance values.

Uncertainty in the $Fm_{large\text{-}blank}$, Fm_{cont}, and m_{cont} values cannot be uniquely determined. In our case, the uncertainty in $Fm_{large\text{-}blank}$ was taken to be:

$$\delta_{Fm_{large-blank}} = \frac{1}{2}Fm_{large-blank} \quad (8)$$

This value encompasses about two-thirds of the variation seen in individual Fm values of large-mass "radiocarbon-free" samples.

For the error in Fm_{cont}, and m_{cont}, an error was assigned to each value such that, after propagation, approximately 68% of the corrected Fm (i.e., Fm_{unkown}) values were within 1 standard deviation of the consensus value resulting in a normal distribution of results. This error determination was done after χ^2 minimization. The darker gray lines in Figures 2

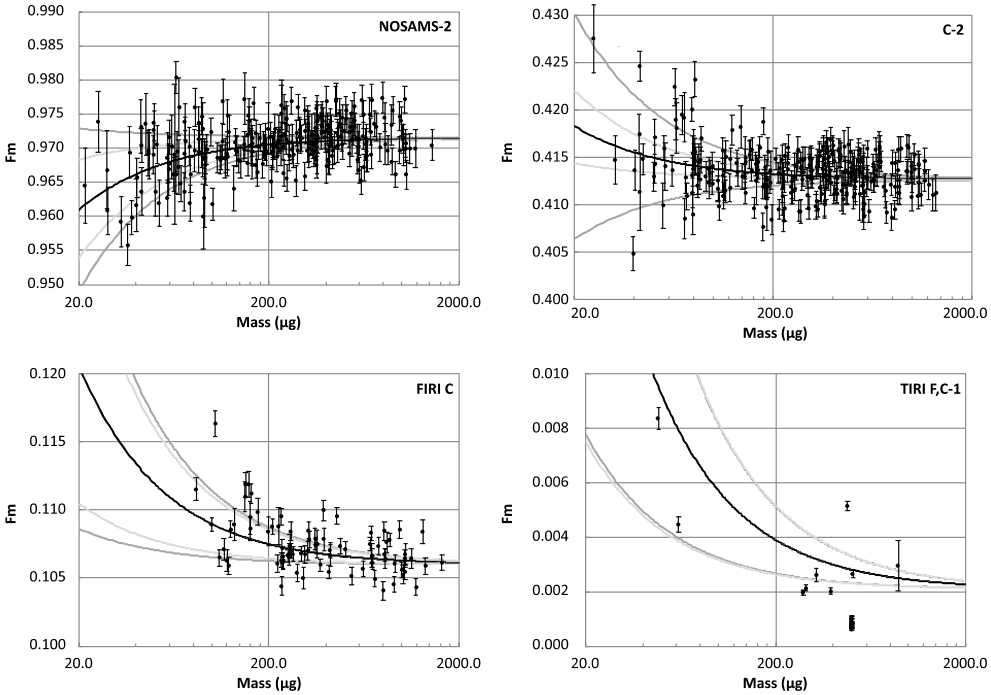

Figure 2 A subset of inorganic secondary standards processed on NOSAMS's "small-sample" line. The black lines are expected results using the blank and mass-balance values listed in Table 1. The gray lines show model sensitivity to the contaminant Fm (dark gray, ±0.41) and mass (light gray, ±0.42 µg).

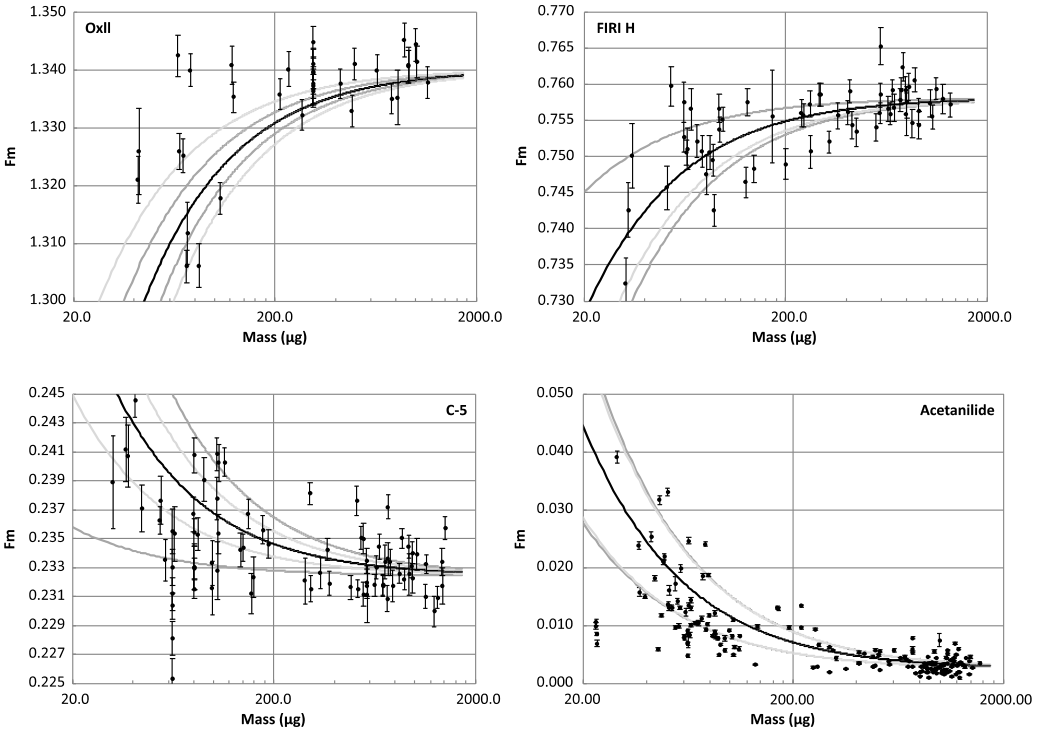

Figure 3 A subset of organic secondary standards processed on NOSAMS's "small-sample" line. The black lines are expected results using the blank and mass balance values listed in Table 1. The gray lines show model sensitivity to the contaminant Fm (dark gray, ±0.18) and mass (light gray, ±0.84 µg).

Table 1 Calculated mass balance and large mass blank values for samples processed on NOSAMS's "small-sample" graphitization line.

	Inorganic samples	Organic samples
Fm of blank	0.61 ± 0.41	0.44 ± 0.18
Mass of blank (μg)	0.60 ± 0.42	2.10 ± 0.84
Fm of large mass blank	0.0020 ± 0.0010	0.0024 ± 0.0012

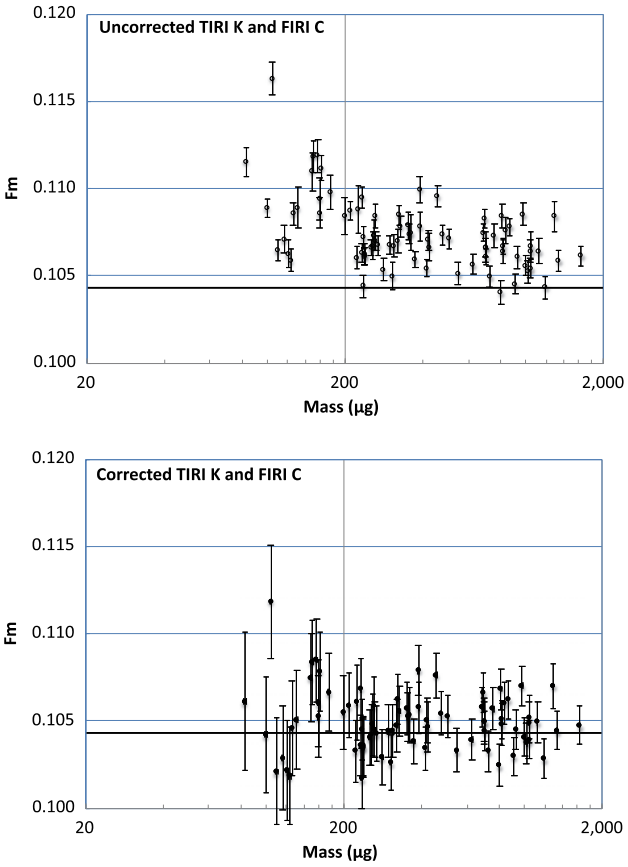

Figure 4 Uncorrected and corrected data from TIRI K and FIRI C (Turbidite Carbonate). The solid line is the consensus value of Fm = 0.1043.

and 3 show the sensitivity of expected $Fm_{measured}$ to uncertainty in the Fm of the contaminant. Light gray lines show the sensitivity of expected $Fm_{measured}$ to uncertainty in the mass of the contaminant.

Figure 4 shows uncorrected and corrected data from measurements of the inorganic TIRI K / FIRI C (Turbidite Carbonate) sample material using the $Fm_{large\text{-}blank}$, Fm_{cont}, and m_{cont} values

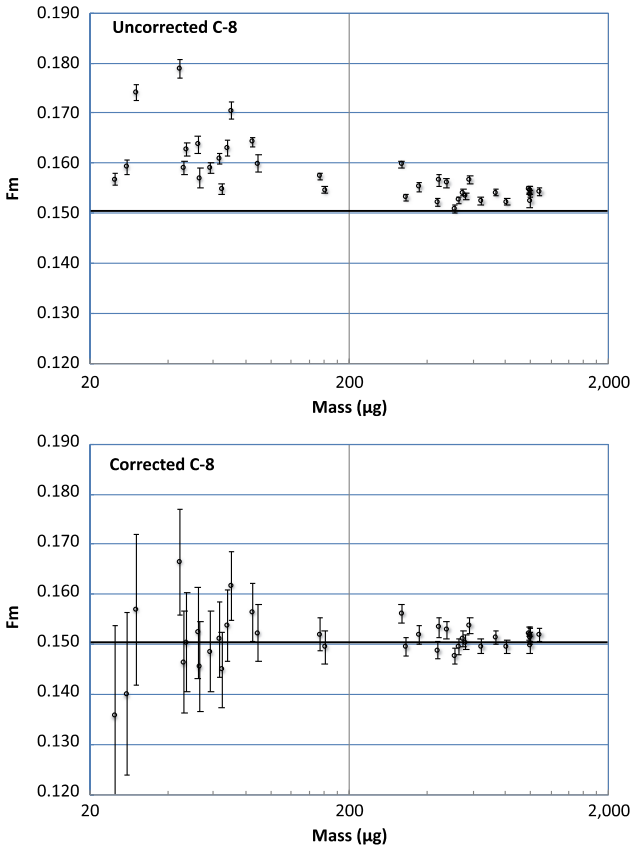

Figure 5 Corrected and uncorrected data from the organic sample C-8 (Oxalic Acid). The solid line is the consensus value of Fm = 0.1503.

for inorganic samples listed in Table 1. Likewise, Figure 5 shows uncorrected and corrected data from measurements of the C-8 (Oxalic Acid) sample materials using the $Fm_{large\text{-}blank}$, Fm_{cont}, and m_{cont} values for organic samples listed in Table 1. Error bars for corrected Fm values (i.e., $Fm_{unknown}$) are much larger than the original $Fm_{measured}$ error bars due mainly to the uncertainty of both Fm_{cont} and m_{cont}. To assess the quality of the blank values, Table 2 lists χ^2's of two indicative sub-samples calculated before and after blank correction. These χ^2's are not the same as those used to derive the three-parameter model (i.e., Equation 7). This is a separate calculation and these χ^2 values should be judged quantitatively only in relative sense in that the corrected values listed in Table 2 are artificially reduced by the boost in the uncertainties of $Fm_{large\text{-}blank}$, Fm_{cont}, and m_{cont}.

While the model works to the extent that broad bias in reported $Fm_{unknown}$ values at low sample mass is removed, it fails to describe the substantial variability observed in the raw (i.e., $Fm_{measured}$) data. While this variability is not totally understood, the assigned uncertainties in the blank values (i.e., $\delta_{Fm_{large\text{-}blank}}$, $\delta_{Fm_{cont}}$, and $\delta_{m_{cont}}$) significantly increases the reported uncertainties on unknowns (i.e., $\delta_{Fm_{unknown}}$) and compensates for the variability observed in the raw data.

Table 2 Reduced chi-squared statistics calculated before and after blank and mass balance blank correction. See text.

	TIRI K and FIRI C (Turbidite Carbonate)	C-8 (Oxalic Acid)
χ^2 $Fm_{measured}$	26.58	60.38
χ^2 $Fm_{corrected}$	1.14	1.01
N	80	40

For samples with masses >100 µg carbon we do not apply a mass balance correction. For those samples the mass dependent correction is relatively small, and we find that more accurate results are obtained by applying only a blank that is measured concurrently with the unknown sample as opposed to a long-term average blank. Additionally, the values listed in Table 1 are not valid for all sample types. For example, ^{14}C analysis of tree rings involves cellulose extraction chemistry, and would require a process specific determination of the associated blank.

NOSAMS also measures "ultra-small" samples. Ultra-small samples are typically defined as those samples having a carbon mass less than ~25 µg carbon. A similar exercise for estimating Fm_{cont}, m_{cont}, and Fm_{blank} for these mass samples was conducted. Although not presented here, results similar to those listed in Table 1 were obtained. (Shah-Walter 2015).

SUMMARY

We have developed a formula that fits the observed mass dependency in measured Fm values. Using long-term measurements of quality control samples, we have modeled the Fm and mass of the blank added during sample processing and AMS measurement. Long term measurements also incorporate short term (wheel-to-wheel) variability in the blank. Different sample types were used to assess the blank added for different sample preparation methods. Applying the mass dependent and mass independent blank values, we have corrected measured Fm values of secondary standards to significantly improve their agreement with consensus values in the mass range 25 µg < mass < 100 µg.

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